

Effect of an Allyl Pretreatment of Starch on the Grafting Efficiency and Properties of Allyl Starch-g-Poly(acrylic acid)

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ABSTRACT: Starch was pretreated with allyl etherification to enhance the grafting efficiency of the copolymerization of granular starch with acrylic acid and to improve the properties of starch-g-poly(acrylic acid) used as a warp sizing agent. The graft copolymerization was carried out in an aqueous dispersion with ferrous ammonium sulfate and hydrogen peroxide as initiators. Through the introduction of allyl groups into starch before the copolymerization, the grafting efficiency could evidently be enhanced, and properties such as fiber adhesion and film behaviors of the copolymer were improved. The pretreatment was capable of enhancing the grafting efficiency by

about 10–20% when the degree of substitution of allyl starch ranged from 0.011 to 0.037. The adhesion and film behaviors also depended on the modification extent of the starch pretreatment and on the grafting ratio of the copolymer. The adhesion reached a maximum at a degree of substitution of 0.025, and the film behaviors were best when the degree of substitution ranged from 0.011 to 0.025. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2822–2829, 2009

Key words: adhesion; fibers; graft copolymers; polysaccharides

INTRODUCTION

Starch possesses many advantages, such as abundant sources, low production costs, and better biodegradability.¹ However, natural starch shows poor adhesion to fibers, and the film is rigid and brittle. Numerous experiments and industrial trials have demonstrated that chemical modification constitutes a powerful means of improving starch serviceability.^{2,3} It has been reported that sizing properties of starch can be improved through graft copolymerization.^{4,5} Presently, some kinds of starch graft copolymers are industrially produced by Sichuan Jiahao Chemical Industry Co., Ltd. (Sichuan, China),⁶ and used in China as warp sizing agents for high-count and high-density fabrics.

Increasing the grafting efficiency is an effective way of improving the properties of starch graft copolymers and reducing their preparation costs.^{7,8} However, the graft copolymerization of starch with vinyl monomers is always accompanied by the homopolymerization of vinyl monomers as reac-

tants. The homopolymerization is a side reaction of the copolymerization. It can be imagined that, through the introduction of polymerizable double bonds into starch molecules before graft copolymerization, the double bonds can be incorporated into copolymeric chains when they meet propagating activated chains. If a propagating activated chain that initiates homopolymerization meets with the double bonds, the original homopolymerization will be converted into copolymerization. Therefore, some portion of the homopolymers will become graft copolymers, and the grafting efficiency can be enhanced. Consequently, the grafting ratio will be correspondingly enhanced with the increase in the efficiency. It has been elucidated that the homopolymers are inferior to the copolymers in serviceability.⁹ As a result, increasing the grafting efficiency enhances the serviceability of the products. On the other hand, if the grafting ratio is similar, the enhancement of the grafting efficiency decreases the required amounts of the monomers, and this reduces the production cost.

To enhance the grafting efficiency of starch graft copolymers, previous investigators have tried to obtain reasonable technological parameters for the copolymerization,^{10,11} but no researcher has tried to adopt starch pretreatment through the introduction of polymerizable double bonds before the copolymerization. In these approaches, starch graft

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copolymers are prepared through the grafting of a series of vinyl monomers onto natural starch or starch containing no double bonds. Mostafa and El-Sanabary¹² reported that sizing properties of starch could be evidently improved through the grafting of a quantity of acrylic acid onto starch.¹² By the introduction of polymerizable double bonds onto starch through the pretreatment of allyl etherification, the grafting efficiency, sizing properties such as fiber adhesion, and film behaviors of starch graft copolymers could be enhanced. Therefore, the impact of the modification on the grafting efficiency and sizing properties was investigated. It is necessary to find a way to efficiently increase the grafting efficiency and improve the properties required in sizing operations.

EXPERIMENTAL

Materials and reagents

Commercial cornstarch with a moisture content of 13.8% and an apparent viscosity of 52 mPa s (6%, 95°C) was supplied by Yixing Starch Factory (Jiangsu, China). The corn starch was refined before being used for the allyl treatment.¹³ All reagents in the experiments were pure grades.

All-polyester roving (361 tex, twist factor = 49.8) and pure cotton roving (456 tex, twist factor = 128) were supplied by Yizheng Chemical Fiber Co., Ltd. (Jiangsu, China), and Qingfeng Textile Co., Ltd. (Jiangsu, China), respectively. The polyester fibers in the all-polyester were 38 mm × 1.73 dtex, and the cotton fibers in the pure cotton roving were 27.44 mm × 1.91 dtex.

Allyl pretreatment of starch

Before the allyl pretreatment, the refined cornstarch was hydrolyzed to reduce its excessive viscosity.¹⁴ Then, 162 g (dry weight) of hydrolyzed cornstarch was mixed with a distilled water/isopropyl alcohol medium (20 : 80 w/w) to form a 30% suspension. The suspension was transferred into a 1000-mL, three-necked flask. Two grams of sodium hydroxide dissolved in 50 mL of distilled water was added to the flask. The mixture was heated to 30°C and stirred continuously with a mechanical stirrer. Half an hour later, an allyl chloride/isopropyl alcohol solution was charged into the flask, and the reaction remained constant at 30°C for 24 h. The starch was filtered, redispersed in a distilled water/alcohol solution (18 : 82 v/v), and neutralized with dilute hydrochloric acid (4 mol/L) to pH 6–7. Finally, the product was filtered, washed thoroughly with distilled water, dried at 50°C, pulverized, and sieved with a 100-mesh sieve.

Graft copolymerization

Allyl starch (130 g) and 390 mL of distilled water were mixed, and the mixture was adjusted to pH 3–4 with dilute sulfuric acid. The suspension was transferred into a 500-mL, four-necked flask equipped with a paddle-type stirrer and three dropping funnels. The flask was maintained in a thermostatically controlled water bath at 30°C. A 0.5% ferrous ammonium sulfate solution and a 0.8% hydrogen peroxide solution were used as initiator solutions. The molar ratio [H₂O₂/FeSO₄·(NH₄)₂SO₄/anhydroglucose unit of starch] was 20/1/1000. After nitrogen gas was charged into the flask for 30 min, acrylic acid and the initiator solutions were added continuously through dropping funnels at such a speed that the addition was completed uniformly in 20–30 min. The graft copolymerization was carried out under vigorous stirring and under the protection of a nitrogen atmosphere for 3 h. After the addition of 3.5 mL of a 2% paradioxybenzene solution to terminate the copolymerization, the product was neutralized to pH 6–7, filtered, washed thoroughly with distilled water, dried at 50°C, pulverized, and sieved with a 100-mesh sieve.

Characterization of allyl starch

The amount of introduced allyl groups was measured by titrimetric analysis. The double bonds of allyl groups reacted with bromine, and the residual bromine was then reacted with iodine. The excessive iodine was titrated with sodium hyposulfite.¹⁵ The degree of substitution (DS) was calculated as follows:

$$DS = \frac{162x}{79.904 \times (2 - 0.5006x)} \quad (1)$$

$$x = \frac{(V_1 - V_2) \times C \times 0.0799}{W} \times 100 \quad (2)$$

where x (%) is the bromine value; V_1 (mL) and V_2 (mL) are the volumes of the standard sodium hyposulfite solution consumed in blank and sample titration, respectively; C (mol/L) is the concentration of the sodium hyposulfite solution; and W (g) is the dry weight of the starch sample.

Characterization of the grafted starch

A purification process was applied to remove the homopolymers [poly(acrylic acid) (PAA)] from the starch products. The samples were washed with distilled water to such an extent that no homopolymer existed in the filtrate. The method used to examine the homopolymer in the filtrate was in accordance with Bayazeed et al.'s method.¹⁶

Determinations of residual monomers and double bonds of the starch graft copolymers were performed by titration of the double bonds of residual monomers in the filtrate and the purified copolymers,¹⁵ respectively. The percentage of double bonds that reacted and the monomer conversion were calculated with eqs. (3) and (4), respectively:

$$\text{Percentage of double bonds that reacted (\%)} = \frac{D_1 - D_2}{D_1} \times 100 \quad (3)$$

$$\text{Monomer conversion (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \quad (4)$$

where D_1 and D_2 are the amounts of double bonds of starch before and after graft copolymerization, respectively, and W_1 and W_2 are the weights of the charged acrylic acid monomer and the residual monomers, respectively.

The amount of PAA grafted onto starch molecules was measured by the titration of carboxyl in PAA branches. Sodium carboxyl in grafted branches was initially converted into carboxyl acid with a dilute HNO_3 solution. Then, an excessive sodium hydroxide standard solution was added to neutralize the carboxyl acid. Finally, the residual sodium hydroxide was titrated with a hydrochloric acid standard solution. The titration method and calculation were described by Zhang.¹⁷

The grafting ratio and efficiency were calculated with the following equations:^{18,19}

$$\text{Grafting ratio (\%)} = \frac{W_3}{W_0} \times 100 \quad (5)$$

$$\text{Grafting efficiency (\%)} = \frac{W_3}{W_1 - W_2} \times 100 \quad (6)$$

where W_3 and W_0 are the weights of PAA grafted onto the starch molecules and original starch, respectively.

Viscosity measurement

An NDJ-79 viscometer (Electrical Machinery Plant of Tongji University, Shanghai, China) was used to determine the apparent viscosity and viscosity stability of allyl starch-g-poly(acrylic acid) (AS-g-PAA). A starch sample was suspended in distilled water to form a 6% (w/w) dispersion. The dispersion was heated to 95°C and maintained at that temperature for 1 h under mechanical stirring. The apparent viscosity of the gelatinized starch paste was measured at 95°C with a shear rate of 344 s^{-1} . The viscosity stability of the paste denoted the percentage of viscosity invariability over a period of 2.5 h at 95°C.¹⁴ The stability was measured from 1 to 3.5 h after starch gelatinization. Meanwhile,

the viscosity values were taken every 30 min, and the stability was calculated as follows:

$$\text{Viscosity stability of starch paste (\%)} = \left(1 - \frac{V_{\max} - V_{\min}}{V}\right) \times 100 \quad (7)$$

where V is the apparent viscosity of the paste and V_{\max} and V_{\min} are the maximum and minimum readings of the viscosity over the period, respectively.

Measurement on the adhesion and film behaviors

A 1% (w/w) starch/distilled water dispersion was cooked at 95°C with mechanical stirring for 1 h. Then, the roving, which had been carefully wound onto a special frame, was impregnated with cooked starch paste for 5 min at the same temperature. The impregnated roving samples were hung, dried in air, and collected for the drawing test. The failure loads of the roving were determined.¹⁴ It is the failure load that is adopted to exhibit the adhesion of a sizing agent to fibers.

The starch film was cast with 400 g of starch paste (6% w/w). The preparation of starch paste was performed in the same way as the experiment for the starch viscosity measurement. The paste was poured onto a 650 mm × 400 mm polyester film spread onto a glass plate of the same size and dried at 65% relative humidity and 20°C. The film behaviors were measured.¹⁴

RESULTS AND DISCUSSION

Evidence of grafting

The Fourier transform infrared spectra of purified natural starch, allyl starch, and starch-g-PAA are illustrated in Figure 1. An absorption peak appears

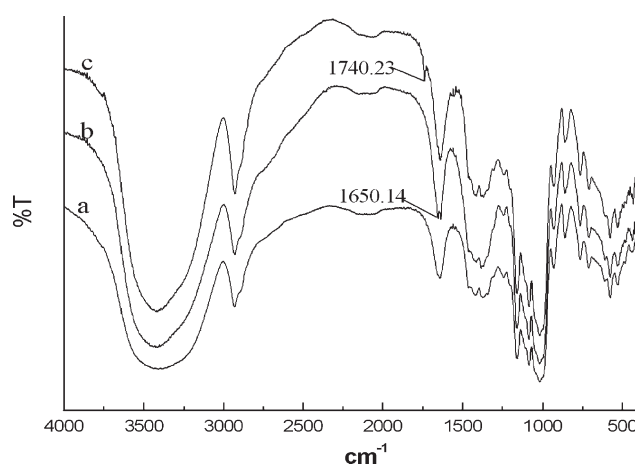


Figure 1 Fourier transform infrared spectra of (a) natural starch, (b) pure allyl starch, and (c) purified S-g-PAA.

TABLE I
Influence of the Pretreatment on Graft Copolymerization

Starch sample	DS	Grafting efficiency (%)	Grafting ratio (%)	Monomer conversion (%)	Reacted double bonds (%)
S-g-PAA	—	53.2	5.21	98.0	—
AS-g-PAA	0.0046	62.7	6.19	98.7	92.0
	0.011	64.3	6.38	99.2	90.2
	0.025	68.3	6.53	95.7	91.3
	0.037	73.7	7.18	97.4	93.6
	0.068	74.0	7.04	95.1	94.4

The weight ratio of the monomers to starch was 10%.

at 1650 cm^{-1} in the infrared spectrum of allyl starch, corresponding to the stretching vibration of double bonds. It demonstrates the existence of allyl groups. For the spectrum of purified grafted starch, the peak at 1740 cm^{-1} corresponds to the carbonyl stretching vibration, which proves the existence of grafted branches.

Influence of the pretreatment on graft copolymerization

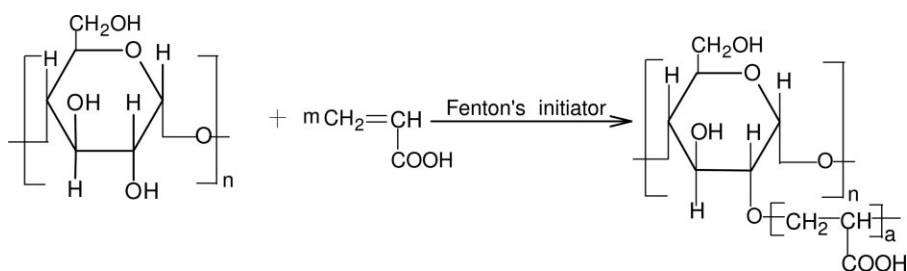
The grafting efficiency and ratio of the prepared AS-g-PAA are shown in Table I. In comparison with the starch-g-poly(acrylic acid) (S-g-PAA) prepared with nonpretreated starch, the grafting efficiency and ratio obviously increase with the introduction of polymerizable double bonds onto the starch before graft copolymerization. The two indices increase progressively with the DS value increasing. Moreover, all the monomer conversions are above 95%.

When starches not containing double bonds are used for the copolymerization with Fenton's initiator [H_2O_2 and $\text{FeSO}_4\cdot(\text{NH}_4)_2\text{SO}_4$], the grafted branches that are produced are connected with the starch backbones only through oxygen because the graft copolymerization is initiated by the abstraction of active hydrogen from starch hydroxyls. The copolymerization^{4,12} can occur as shown in Scheme 1. If the starch used for the copolymerization has been allyl-etherified, the polymerizable double bonds that are introduced may meet with the propagating chain radicals. The bonds will be incorporated into the

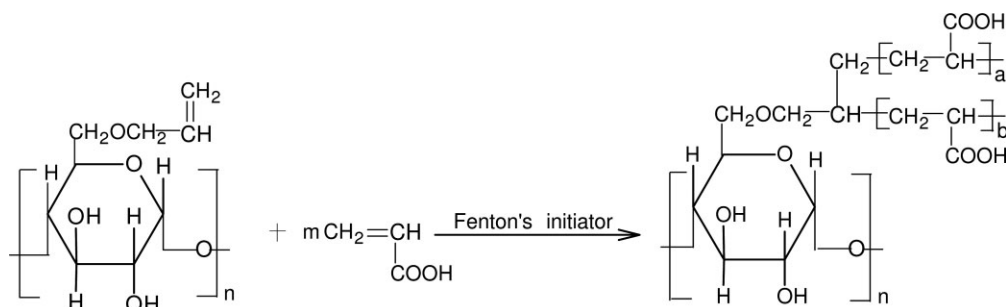
propagating chains, and the copolymerization can occur as shown in Scheme 2. In this case, the graft copolymerization shown in Scheme 1 also occurs. Therefore, grafted branches can be connected with the starch backbones through both double bonds and oxygen if allyl starch is used as the reactant of the copolymerization. When a free radical that initiates homopolymerization and produces a homopolymer meets with the double bonds, the starch molecule will be incorporated into the chain. For this reason, the double bonds on starch backbones are capable of partly converting homopolymerization into graft copolymerization. Consequently, the homopolymers formed in the graft copolymerization decrease, and the graft copolymers are enhanced. Titration analysis of the double bonds demonstrates that over 90% of the double bonds react in the graft copolymerization. This suggests that the double bonds have a function in the copolymerization. Therefore, the grafting efficiency and ratio increase by means of the allyl etherification before graft copolymerization. The more double bonds there are, the greater the likelihood is of the propagating chain meeting the double bonds. As a result, the grafting efficiency and ratio of the graft copolymerization increase progressively with the increase in the DS value.

Influence of the pretreatment on the paste viscosity

The influence of allyl etherification on the viscosity and viscosity stability of AS-g-PAA is shown in



Scheme 1 Principle of forming grafted branches connected by oxygen in hydroxyls by Fenton's initiator.



Scheme 2 Principle of forming grafted branches through the double bonds.

Table II. Obviously, increasing the DS value of allyl starch enhances the viscosity of the AS-g-PAA paste. As is well known, crosslinking occurs in polymerization when the degree of functionality of a reactant is more than 2. The crosslinking structure between the molecules of allyl starch after the copolymerization can be described as shown in Scheme 3.

In the copolymerization of starch with vinyl monomers with Fenton's initiator, a grafted branch can be achieved in the position of oxygen through the abstraction of hydrogen from hydroxyls and forms primary active radicals. However, when starch is allyl-esterified, the allyl groups containing double bonds on the starch backbones result in the formation of a grafted branch that is bonded with the groups. These two branches can be grafted onto the same starch molecule. In this case, starch likes the bifunctional reactant, and crosslinking occurs amid the starch.

Carboxyl, as a side group of PAA branches on starch backbones, is hydrophilic and electrostatically repulsive. Therefore, the existence of PAA grafted branches enhances the viscosity of aqueous pastes of starch graft copolymers. With an increase in the DS value, the number of double bonds increases, and this induces the enhancement of the grafting ratio and mild crosslinking. Thus, the increase in the DS value also leads to the increase in the viscosity. Moreover, the viscosity stability increases as the DS value increases. Apparently, this is also due to the mild crosslinking between starch macromolecules. It has been elucidated that the stability is very important for sizing agents because the behavior supplies a base for obtaining a stable size add-on. This indicates that mild crosslinking has a positive influence on the stability.

Effect of the pretreatment on the film behaviors

A warp sizing operation requires starch films to possess characteristics such as appropriate tensile strength, great extension and work to break, and low wear loss. Therefore, it is necessary to evaluate

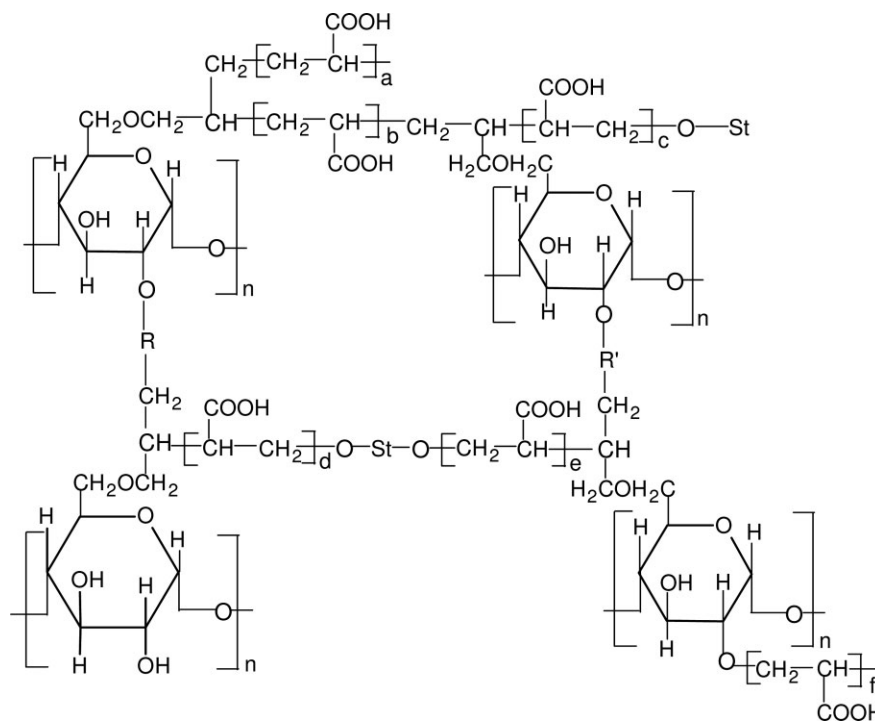
the effect of the pretreatment on the behaviors mentioned previously. The influence of allyl etherification on the behaviors of starch-g-PAA film is shown in Table III. Obviously, the pretreatment improves the film behaviors. With an increase in the DS value, the tensile strength, work to break, and abrasive resistance all increase initially, reach their maximum at DS = 0.011–0.025, and then decrease. The extension decreases when the DS value is over 0.037.

As is well known, the polarity of carboxylic groups is stronger than that of hydroxyls. This implies that the intermolecular force between AS-g-PAA molecules is greater than that between starch molecules. The introduced branches disturb the association of starch hydroxyls and interfere with the regular arrangement of amylose because of their steric hindrance effect, and this makes starch molecules stack loosely. Carboxylic groups are hydrophilic and are capable of absorbing water into starch film. The grafted branches and the absorbed water plays a plasticization role for the film. Furthermore, the introduced branches are flexible in comparison with the starch backbones. The variations are favorable for enhancing either the tensile strength or extension of the film. Consequently, a strong and tough film would be logical for the graft copolymers

TABLE II
Influence of the Pretreatment on the AS-g-PAA Paste Viscosity

Starch sample	DS	Apparent viscosity (mPa s)	Viscosity stability (%)
Acidified starch	—	13.0	84.6
Allyl starch	0.025	6.0	83.3
S-g-PAA	—	15.0	86.7
AS-g-PAA	0.0046	13.0	92.3
	0.011	14.0	92.9
	0.025	14.0	92.9
	0.037	17.0	94.1
	0.068	26.0	94.2

The grafting efficiencies and ratios of the starch samples were the same as those shown in Table I.



Scheme 3 Chart illustrating the formation of crosslinking in the graft copolymerization of allyl starch with acrylic acid. St denotes the starch backbone, whereas R and R' are the PAA branches grafted onto the starch backbone.

when the DS value increases initially. However, as the extent of crosslinking further increases, the water dispersibility of starch will remarkably decrease.²⁰ The decrease is deleterious to the thermal motion of macromolecular chains and to diffusion between particles in the process of film formation. For this reason, the film will become rigid and brittle and the film behaviors will become lower if the modified starch is excessively crosslinked.

Effect of the pretreatment on the adhesion

The starches used in warp sizing applications belong to temporary adhesives. For an adhesive used in bonding fibers, its adhesion to fibers determines its

end use. Therefore, the impact of the pretreatment on the adhesion should be evaluated. The influence of the allyl pretreatment on the adhesion of AS-g-PAA to cotton and polyester fibers is depicted in Figures 2 and 3, respectively. The tensile strength and work to break of the two kinds of sized rovings can be enhanced obviously through allyl etherification and graft copolymerization. The increases in the two indices suggest an improvement of the adhesion. The adhesion increases initially with an increase in the DS value, reaches a maximum at DS = 0.025, and then decreases gradually.

Generally, the cohesive failure of an adhesive joint depends on the mechanical behaviors of adhesive layers between fibers. However, it is impossible to

TABLE III
Effect of the Pretreatment on the Film Behaviors

Starch sample	DS	Tensile strength		Extension		Work to break		Wear loss	
		N/mm ²	CV (%)	%	CV (%)	J	CV (%)	mg/cm ²	CV (%)
Acidified starch	—	27.1	9.41	2.26	12.06	38.4	9.64	0.60	8.33
Allyl starch	0.025	24.6	9.72	2.41	13.28	34.7	8.88	0.43	7.44
S-g-PAA	—	28.3	5.55	1.78	14.17	31.3	7.38	0.49	6.94
AS-g-PAA	0.0046	28.7	6.10	2.55	14.12	42.6	7.28	0.48	7.92
	0.011	35.0	5.71	2.70	13.70	55.8	6.65	0.39	8.89
	0.025	37.1	5.47	2.82	13.48	50.3	6.96	0.46	6.96
	0.037	25.6	6.33	2.71	12.55	35.8	7.40	0.58	8.52
	0.068	24.8	6.74	2.01	14.41	21.5	8.81	0.62	8.06

The grafting efficiencies and ratios of the starch samples were the same as those shown in Table I. CV = coefficient of variation.

strip the adhesive layers between fibers for the determination of their real mechanical behaviors. Fortunately, previous investigation has revealed that a cast film with the same materials can be adopted to estimate the mechanical behaviors.¹⁴ The tensile strength and elongation of an AS-g-PAA film are greater than those of nongrafted starch. This suggests that the branches introduce both toughness and strength to the adhesive layers of AS-g-PAA. Undoubtedly, strong layers favor adhesion to fibers. As elucidated previously, the flexibility is also important for reducing the stress concentration²¹ because the reduction in stress favors an improvement in the adhesion. Therefore, the adhesion of AS-g-PAA to all-polyester and cotton fibers is initially enhanced. However, chemical crosslinking between starch molecules occurs in graft copolymerization because of the introduction of double bonds. It has been elucidated that crosslinking reduces the water dispersibility of starch and that the reduced dispersibility decreases the wetting and spreading of starch paste onto fibers; this lowers the adhesion.²⁰ In addition, an excessive amount of allyl groups results in excessive crosslinking between starch molecules. Our experiments have shown that excessive crosslinking reduces the tensile strength and extension of an AS-g-PAA film abruptly. Therefore, excessive crosslinking makes the layers between fibers brittle and causes the adhesion to decrease seriously. The extent of allyl etherification evidently should not exceed 0.025 on the basis of the adhesion. Further increasing the number of allyl groups produces an adverse effect and reduces the adhesion of AS-g-PAA to both fibers.

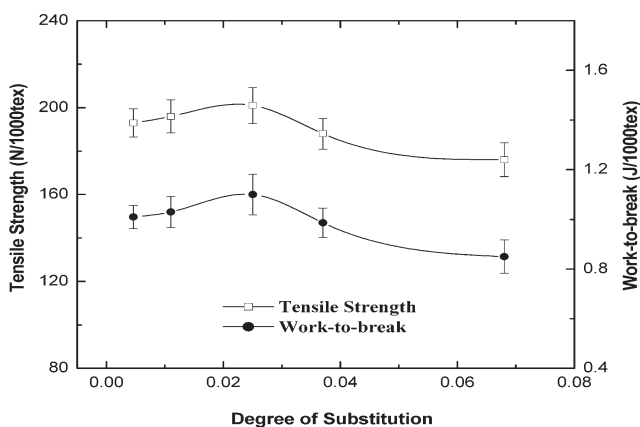


Figure 2 Effect of the pretreatment on the adhesion to pure cotton fibers. The grafting efficiencies and ratios of the starch samples were the same as those in Table I. The tensile strength of the acidified starch, allyl starch, and S-g-PAA was 176, 174, and 188 N/1000 tex, respectively. The work to break of these three kinds of starches was 0.953, 0.933, and 0.989 J/1000 tex, respectively.

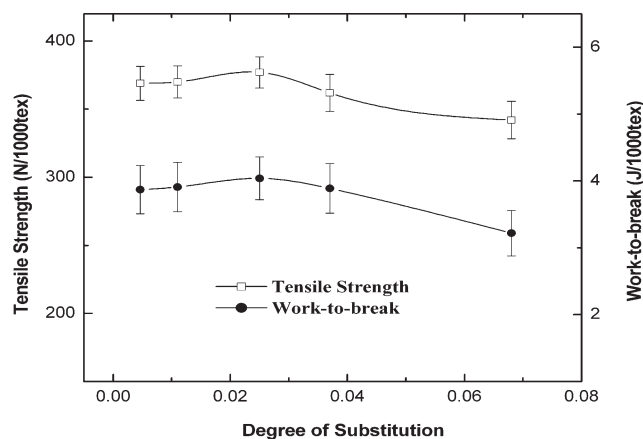


Figure 3 Effect of the pretreatment on the adhesion to all-polyester fibers. The grafting efficiencies and ratios of the starch samples were the same as those in Table I. The tensile strength of the acidified starch, allyl starch, and S-g-PAA was 306, 314, and 366 N/1000 tex, respectively. The work to break of these three kinds of starches was 2.73, 2.84, and 3.83 J/1000 tex, respectively.

CONCLUSIONS

Through the introduction of allyl groups into starch before starch graft copolymerization, the grafting efficiency of graft copolymerization between granular starch and acrylic acid can be enhanced by about 10–20% when the DS value of the allyl starch is in the range of 0.011–0.037. The properties of AS-g-PAA used as the sizing agent also rely on the extent of allyl etherification before the copolymerization. Excessively increasing the modification extent of starch allyl etherification lowers the properties of the copolymers as warp sizing agents. However, extremely reducing the extent does not achieve enough of an effect on the improvement of the grafting efficiency. This implies that the extent of etherification should be chosen according to the improvements in both the properties and grafting efficiency. Properties such as the viscosity, viscosity stability, fiber adhesion, and film behaviors of the copolymers depend on the extent of etherification. The viscosity and viscosity stability increase as the extent of modification increases. The adhesion increases initially with the DS value, reaches a maximum at DS = 0.025, and then decreases. Favorable film characteristics such as tensile strength, extension, work to break, and abrasion resistance can be achieved when the DS value ranges from 0.011 to 0.025. On the basis of the grafting efficiency and properties, the extent of allyl etherification is recommended to be in the range of 0.011–0.025. Our experiments have demonstrated that not only does the allyl pretreatment supply a new way of enhancing the grafting efficiency but it also improves the properties of AS-g-PAA when used as a warp sizing agent.

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